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Negative carbon intensity of renewable energy technologies involving biomass or carbon dioxide as inputs

Wojciech M. Budzianowski *

Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

A R T I C L E I N F O

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A B S T R A C T

Conventional fossil fuel-based energy technologies can achieve efficiency in energy conversion but they are usually completely inefficient in carbon conversion because they generate significant CO_2 emissions to the atmosphere per unit energy converted. In contrast, some renewable energy technologies characterized by negative carbon intensity can simultaneously achieve efficiency in the conversion of energy and in the conversion of carbon. These carbon negative renewable energy technologies can generate useful energy and remove CO_2 from the atmosphere, either by direct capture and recycling of atmospheric CO_2 or indirectly, by involving biofuels. Interestingly, the deployment of carbon negative renewable energy technologies can offset carbon emissions from conventional fossil fuel-based energy technologies and thus reduce the overall carbon intensity of energy systems.

The current review analyzes two groups of renewable energy technologies involving biomass or CO_2 as inputs. The discussions focus on useful techniques which enable to achieve negative carbon intensity of energy while being technologically promising in near-term as well as cost-effective. These analyzes include advanced carbon sequestration concepts such as soil carbon sequestration and CO_2 recycling to useful C-rich products such as fuels and fertilizers. The 'drop-in' of renewable energy is achieved by allowing bioenergy and renewable energies in the form of renewable electricity, renewable thermal energy, solar energy, renewable hydrogen, etc. The carbon negative renewable energy technologies are analyzed and perspectives and constraints of each technology are expounded.

Contents

Abbreviations: AD, anaerobic digestion; BM, biomethane; BS, biosyngas; C, carbon; CCR, CO_2 capture and recycling; CCS, carbon capture and sequestration; CO_2, carbon dioxide; CSP, concentrated solar power; DME, dimethyl ether; E, energy; ECE, energy-related carbon emissions; F-T, Fischer-Tropsch; *G*, Gibbs free energy (J mol^{-1}); GHG, greenhouse gas; *H*, enthalpy (J mol^{-1}); HHV, higher heating value; HPRSS, high-pressure reactive solvent scrubbing; *K*, reaction equilibrium constant; LCA, Life Cycle Assessment; ORFC, oxy-reforming fuel cell; PV, photovoltaics; *R*, universal gas constant (8.314 J mol^{-1} K^{-1}); *S*, entropy (J mol^{-1} K^{-1}); SNG, synthetic natural gas; SOC, soil organic carbon; *T*, temperature (K)

* Tel.: +48 71 3203814.
E-mail address: wojciech.budzianowski@pwr.wroc.pl

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1. Introduction

Conventional fossil fuel-based energy technologies can achieve efficiency in energy conversion but they are usually completely inefficient in carbon (C) conversion, because they generate significant carbon dioxide (CO_2) emissions to the atmosphere per unit energy converted. The emitted CO_2 adversely affects natural C cycles by highly irreversible accumulation in the atmosphere. Namely, the content of CO_2 in the atmosphere is increasing at a rate exceeding 2 ppmv yr^{-1}. It currently reaches the level of around 391 ppmv [1], about 110 ppmv above the pre-industrial average. The expected further rise in atmospheric CO_2 content can pose a significant danger for ocean ecosystem health, i.e. the excess of atmospheric CO_2 can acidify oceans leading to damaging the oceanic biosphere, and consequently, it can reduce the present natural ability of oceans to absorb large amounts of CO_2 from the atmosphere. Besides, a CO_2-induced global warming effect is characterized by significant time delay, i.e. Earth's thermal response lags behind the rise in atmospheric CO_2 by more than five decades. Hence, even when future CO_2 emissions are reduced and atmospheric CO_2 content is stabilized at a certain level, a significant risk exists that Earth's global mean temperature will further rise during forthcoming decades [2]. These effects imply a need for deployment of technologies able to remove CO_2 from the atmosphere. Overall, energy systems must be less CO_2-intensive because otherwise, unwanted irreversible climate changes might occur [3].

Existing energy technologies are characterized by various C intensities. Only limited number of energy technologies can achieve negative C intensity [4]. There are two large groups of such C negative renewable energy technologies. The first group includes biofuels. These technologies make use of the fact that biomass growth is associated with photosynthesis-based uptake of atmospheric CO_2. C negative intensity is achieved when biomass energy conversion is followed by the conversion of C to stable C-rich products such as fuels, fertilizers or food. The negative C intensity can be particularly pronounced when at the end-of-life of these C-rich products the release of C back to the atmosphere is minimized. The second group of technologies utilizes renewable energy to drive the production processes of C-rich fuels from CO_2 captured either in fossil fuel-fired power plants or directly from the atmosphere.

The present review seeks approaches which are suitable for renewable energy systems and can significantly negate C intensities of energy. The main idea behind current approaches is to avoid or minimize the use of cost-intensive technologies involving C storage in geological formations. Instead, advanced and more cost-effective methods for achieving negative C emissions are addressed. The main focus is thus on two C management technologies: (i) soil C sequestration and (ii) CO_2 conversions to fuels and other useful C-rich products.

The review also highlights how some of these routes can offer a valuable opportunity to introduce renewable energy into the existing energy infrastructures. The focus is thus on techniques allowing 'drop-in' of renewable energy into power systems mainly by synthesizing fuels and fertilizers from biomass and CO_2.

National energy systems in many countries involve a significant share of C intensive energy technologies such as fossil fuel-firing, in particular coal [4]. Therefore, expanded deployment of renewable energy technologies designed to achieve C negative intensity looks particularly promising for these energy systems [5]. C negative renewable energy can offset positive C intensity of fossil fuel-based energies and hence the overall C intensity of energy can be significantly reduced. The potential for decarbonization of energy systems through adoption of C negative renewable energy technologies is large because biomass production capacity for energy use remains significant in many regions of the world. Besides, some countries have or can have the excess of renewable energy associated with: (i) intermittent operation of wind and solar farms, (ii) locally excessive renewable energy sources (solar energy in hot climates, high-altitude wind

and many others). This excess of renewable energy can be used to convert CO_2 into useful stable C-rich products. The recycling of C to fuels beneficially offers storage capability for renewable energy. The stored energy can serve a transportation sector as well as it can stabilize energy systems with significant share of renewable energy. Besides, carbon negative renewable energy carries a modest price if we consider total costs to society, i.e. including both subsidies to coal and the negative external economies of coal [6].

The present study analyzes two large groups of renewable energy technologies characterized by C negative intensity of energy: (i) biofuels and (ii) fuels derived from CO_2 and renewable energy. The emphasis is put on technological refinements that increase C negativity of energy, methodologies for 'drop-in' of renewable energy, technological reliability of carbon negative renewable energy systems and their cost-effectiveness.

2. C intensity of energy

Energy-related CO_2 emissions to the atmosphere (*ECE*, in g C) in relation to energy (*E*, in J) are known as the C intensity of energy (*ECE*/*E*, in $\mathrm{g\,C\,J^{-1}}$). The C intensity of energy is often related to primary energy or to useful energy obtained from power cycles.

2.1. C intensity of primary energy

For fossil fuel-derived energy C intensity of primary energy depends on the content of C and primary energy embedded in these fossil fuels. For instance, high-grade coal has C intensity of primary energy about $2.8 \times 10^{-5}\,\mathrm{g\,C\,J^{-1}}$ while high-methane content natural gas has C intensity of primary energy about $1.35 \times 10^{-5}\,\mathrm{g\,C\,J^{-1}}$. According to IEA's statistics, global C intensity of total primary energy supply in 2009 was $1.54 \times 10^{-5}\,\mathrm{g\,C\,J^{-1}}$ [7]. This value reflects CO_2 emissions from fuel combustion only and includes a significant share of low-carbon energies such as nuclear, hydro and biofuels. The latter explains why the present global C intensity of primary energy mix is close to that of natural gas.

2.2. C intensity of useful energy

C intensity of energy can also be related to useful energy obtained from power cycles. In this case the C intensity of useful energy depends again on the content of C and energy in the fuel and, additionally, on the efficiency of conversion of fuel energy to useful energy. Hence, the C intensity of useful energy reflects the environmental efficiency of the use of primary energy. For instance, when useful energy in the form of electricity is generated in a coal-fired power plant with electricity-to-coal efficiency lower than 40%, the attained C intensity of useful energy is as high as $7 \times 10^{-5}\,\mathrm{g\,C\,J_e^{-1}}$. Similarly, natural gas-fired electric power plants also have significantly higher C intensity of useful energy than C intensity related to primary energy, i.e. about $3.4 \times 10^{-5}\,\mathrm{g\,C\,J_e^{-1}}$.

Interestingly, renewable electricities such as wind or hydro have very low C intensities of useful energy (often well below $0.4 \times 10^{-5}\,\mathrm{g\,C\,J_e^{-1}}$ even when all indirect CO_2 emissions are accounted for), i.e. the majority of renewable electricity technologies is nearly C neutral [4]. Therefore, when energy mix in a given national energy system has a significant share of renewable energy, the attained C intensity of useful energy can be particularly low. McCollum et al. [8] have estimated that the present California's C intensity of electricity is $2.5 \times 10^{-5}\,\mathrm{g\,C\,J_e^{-1}}$. This C intensity of electricity is slightly lower than the C intensity of natural gas-derived electricity because California's electricity mix is mostly based on natural gas and clean hydro power. In contrast, in economies utilizing mostly coal-derived electricity and additionally having relatively inefficient electric coal-fired power plants, the attained C intensity of electricity can be as high as $7.5 \times 10^{-5}\,\mathrm{g\,C\,J_e^{-1}}$ [4].

2.3. C intensity of renewable energy involving biomass or CO_2 as inputs

The assessment of C intensity of renewable energy involving biomass or CO_2 as inputs is far more complex. The central complexity arises from the fact that biomass and CO_2 have embedded C. The embedded C can be either derived from the atmosphere, e.g. through photosynthesis, or it can be captured in power plants and hence prohibited from releasing to the atmosphere. Therefore, when a renewable power cycle converts biomass or CO_2 to secondary C-rich fuels, the net removal of C from the atmosphere is attained. Another complexity is associated with indirect energy and CO_2 emissions. The indirect emissions occur during the production and transportation steps of biomass and equipment needed to generate renewable power.

These complexities are addressed in Fig. 1 which provides suitable terminology. Fig. 1 defines inputs, indirect energy and C emissions, useful secondary products and unwanted wastes for both renewable energy and C commodities.

Further explanations are given in Fig. 2. Fig. 2 introduces an explanatory power cycle involving the conversion of energy and C. Fig. 2 demonstrates that energy and C are always conserved in all power cycles. The considered energy input includes either primary or secondary energy or both. Energy input can be 100% renewable, e.g. wind electricity, solar thermal energy, renewable hydrogen. C input includes C either originating from the

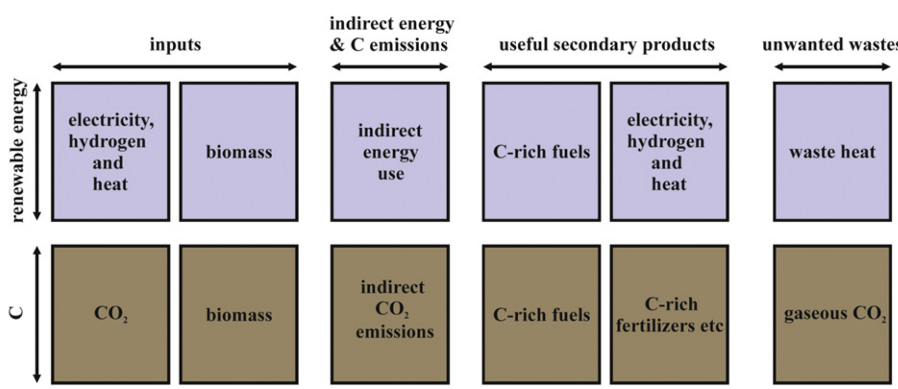


Fig. 1. Terminology for renewable energy and C commodities.

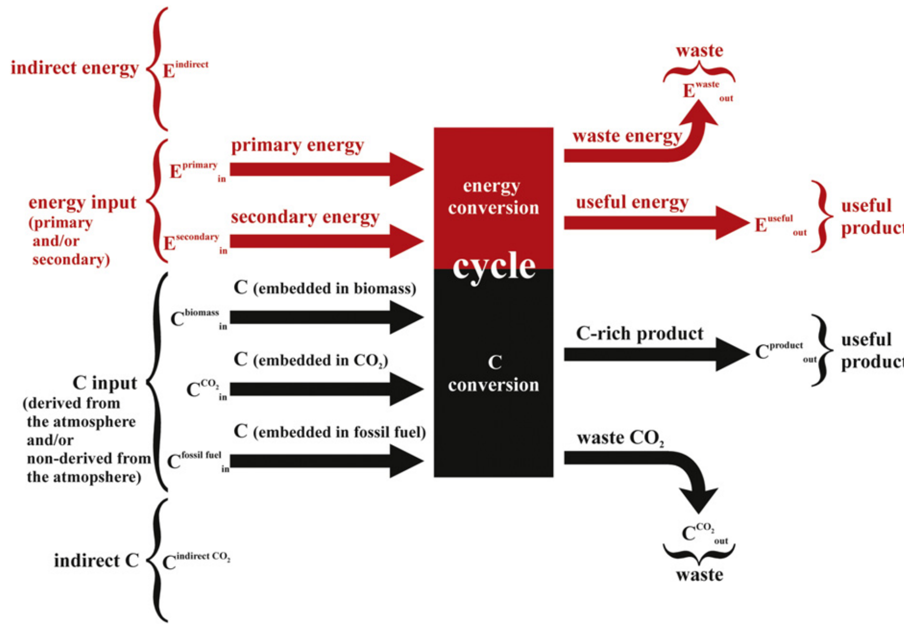


Fig. 2. Explanatory power cycle involving the conversion of energy and C.

atmosphere (biomass or CO_2) or non-originating from the atmosphere (e.g. fossil fuels) or both. C input can include C embedded in biomass, C embedded in CO_2 and/or C embedded in fossil fuel or any combination of them. C input can also be 100% renewable, e.g. based on biomass C. This power cycle can generate various forms of useful energy such as electricity or mechanical energy etc. Main useful C-rich products can be fuels, fertilizers, etc. Inefficiencies encountered in all power cycles always lead to the generation of unwanted waste streams of both energy and C. Typical waste energy takes the form of low temperature streams having negligible exergy content while waste C takes the form of gaseous CO_2. Both these unwanted wastes are released from the cycle to the atmosphere. Additionally, Fig. 2 considers indirect energy and CO_2 emissions. These indirect energy and C are always needed to generate power. They originate from e.g. cultivation and transport of biomass, manufacturing of wind turbines or solar panels, operation and maintenance of power plants, fuel provision, etc.

The explanatory power cycle given in Fig. 2 is useful to understand the balance of atmospheric C. It is seen that net atmospheric C emissions equal to C emissions to the atmosphere ($C_{out}^{CO2}+C^{indirect\ CO2}$) minus C removals from the atmosphere ($C^{biomass}{}_{in}+C_{in}^{CO2}$). Therefore, C intensity of useful energy in this explanatory cycle can be defined as the net atmospheric C emissions in relation to useful energy obtained in this cycle E_{out}^{useful}

$$\frac{ECE}{E}=\frac{C^{CO2}{}_{out}+C^{indirectCO2}-C^{biomass}{}_{in}-C^{CO2}{}_{in}}{E^{useful}{}_{out}} \tag{1}$$

From Eq. (1) it can be clearly deduced that when any renewable power cycle has C input in the form of biomass or CO_2 ($C_{in}^{biomass}+C_{in}^{CO2}$) and when this C input is converted to C-rich products, then little waste CO_2 is released from this power cycle to the atmosphere and consequently it is likely that the attained C intensity of useful energy might be negative. Eq. (1) also explains why fossil fuels are so C positive: fossil fuels derives no C from the atmosphere but simultaneously their combustion generates significant amount of CO_2 released to the atmosphere, i.e. C_{out}^{CO2} is significant. Further, Eq. (1) indicates that when biomass production is associated with significant indirect CO_2 emissions ($C^{indirect\ CO2}$), then these C emissions can negate the benefits associated with biomass C input ($C_{in}^{biomass}$). This can be the case for some biofuels which require energy intensive cultivation.

Various existing and emerging renewable energy technologies can achieve C intensities of energy ranging from positive to negative values. Two groups of renewable cycles are particularly promising as having great potential to achieve negative C intensity of energy: (i) biofuels and (ii) fuels derived from CO_2 and renewable energy. When such renewable power cycles are designed in a practical manner, they can generate useful energy and additionally value-added C-rich products. This review paper explains how to design renewable power cycles in order to achieve negative C intensity of energy.

3. Strategies for C sequestration

The key objective of C sequestration is stabilizing the content of C in the atmosphere. Current C emissions to the atmosphere are around 8 Pg C yr^{-1}. To sequester such huge amounts of C, C sequestration technologies must be massive.

There are two main ideas behind massive C sequestration. The first idea is associated with capturing of C derived from fossil fuel combustion and the second idea is associated with capturing directly atmospheric C. The captured C must be further permanently stored in Earth's C reservoirs. Alternatively, the captured C can be recycled in order to significantly delay the release of C to the atmosphere.

Below, three strategies for massive C sequestration are introduced: (i) the capture of atmospheric CO_2 by terrestrial plants followed by C storage in vegetation and soil, (ii) CO_2 capture followed by C recycling, and (iii) CO_2 capture followed by CO_2 storage in geological formations. The strategies (i) and (ii) are more promising for integration with renewable energy technologies and hence are in focus of the current study.

3.1. C sequestration in vegetation and soil

C sequestration can be achieved through combining biological CO_2 capture and storage in vegetation followed by C storage in soil. Biological CO_2 capture is achieved during solar energy-driven photosynthesis. During the photosynthesis, plants efficiently

capture and store C as biomass. Promising strategies include afforestation and enhanced cultivation of various energy crops. Biosphere has great potential to store C because it is currently storing 560 Pg C, i.e. 72% of C present in the atmosphere [9].

Further, a non-harvested part of C originally stored by plants is retained at biomass cultivation sites and naturally enriches soil C. Soil is the fifth largest C reservoir on Earth with two 500 Pg C, i.e. 325% of the present atmospheric C content [9]. Storing C in agricultural or forest soils builds up soil organic matter and improves physical and chemical properties of soils, which all have benefits for crop production.

The potential of C storage in soil can be further enhanced by fertilizing soils with biogas-derived digestate, biomass pyrolysis-derived biochar and agricultural residues which beneficially recycle nutrients and minimize the use of conventional mineral fertilizers. Liang et al. [10] have pointed out in their 15 years in-field experiment that soil fertilization with organic fertilizers such as farmyard manure has beneficial effect on soil organic C content mainly in the first 30 cm of soil. Therefore, agricultural practices such as cultivation of plants with long roots might be needed to enhance penetration of soil C to deeper layers of soil. Besides, shifting of soil organic C to stable carbonate minerals (e.g. calcium carbonate) which can precipitate naturally or be enhanced by e.g. microorganisms or addition of Ca-rich minerals to soil [11] can further increase the potential of soil C sequestration.

3.2. CO_2 capture and recycling (CCR)

It is likely that large amounts of CO_2 will be available in near future from capture processes in fossil fuel-fired power plants. Therefore, CO_2 can be a zero cost or even with negative value feedstock for innovative C conversion processes. Several opportunities exist for the recycling of captured C to fuels, fertilizers and chemicals. Fuels have the largest market and hence CO_2-derived fuels offer the greatest promise for C recycling. Fertilizers are also promising because the expected expanded production of energy crops can significantly increase the demand for fertilizers in near-term, e.g. according to Han et al. [12] the US fertilizers market can increase by a factor of 5.5 during the 1997–2030 period in the case of rapid development of liquid biofuel production and the dominant use of mineral fertilizers.

CO_2 can be captured by using several relatively mature technologies with proved economics. Additionally, several emerging technologies are at pilot scale [13–17]. The CO_2 recycling step is more challenging, because its economics strongly depend on the value (or negative value) of CO_2, and the availability (and cost) of renewable energy as well as renewable hydrogen. The area of CO_2 capture followed by chemical recycling to fuels, fertilizers and chemicals is a very active R&D sector, and it can represent a challenging possibility for companies to develop complementary strategies to reduce CO_2 emissions [18].

3.3. CO_2 capture and storage (CCS) in geological formations

CO_2 capture and storage in geological formations is most conventional option for C management. It is likely that the deployment of this technology might be also necessary in order to stabilize CO_2 in the atmosphere. However, this third option is relatively unsuitable for 'drop-in' of renewable energy technologies and therefore it is not in the focus of the present study. Besides, geological storage of CO_2 rather does not allow for value-added C management, i.e. it is more difficult to obtain value-added products in addition to C storage in geological formations. Consequently, the current review put emphasis on (i) C sequestration in vegetation and soil and on (ii) CO_2 capture and recycling as being more promising for carbon negative renewable energy technologies.

4. 'Drop-in' of renewable energy

C negative renewable energy technologies must be suitable for 'drop-in' of renewable energy. This 'drop-in' of renewable energy can be achieved differently in bioenergy technologies involving C sequestration in vegetation and soil and differently in non-biomass-based renewable energy technologies involving CO_2 capture and recycling. As indicated in Section 3.3 conventional CCS technologies are usually less suitable for 'drop-in' of renewable energy.

4.1. C negative biofuels

For this first group of C negative renewable energy technologies the 'drop-in' of renewable energy is associated with natural solar energy storage by biomass during photosynthesis. Therefore, little or no renewable energy must be provided for capturing CO_2 from the atmosphere because this process occurs naturally. Similarly, during biomass conversion steps little additional renewable energy is needed because the energy content of biomass can ensure the efficient conversion of biomass even when high-temperature biomass conversion processes are employed. Nonetheless, when the 'drop-in' of renewable energy is allowed, greater quantities of C-rich products can be produced and less waste CO_2 is emitted and hence more negative C intensity of useful energy can be attained.

4.2. C negative fuels derived from CO_2 and renewable energy

For this second group of C negative renewable energy technologies the 'drop-in' of renewable energy is usually more complex. CO_2 capture needs renewable energy either in the form of electricity (e.g. in electrochemical methods), thermal energy (e.g. in sorption methods to regenerate sorbents) or compression work (e.g. in membrane methods [19]).

During recycling of captured CO_2 the minimized consumption of renewable energy is central for ensuring cost-effectiveness of the entire technology. Renewable energy is needed in various forms such as concentrated solar power (e.g. in solar thermochemical cycles), renewable hydrogen (e.g. in CO_2 hydrogenation), renewable electricity (e.g. in electrochemical methods), heat (e.g. in CO_2 reforming) and compression work (e.g. in high-pressure methanol synthesis reactors).

Typical C negative renewable power cycles allow for 'drop-in' of renewable energy in various forms. For instance, hydrogenation of CO_2 to methanol needs thermal energy for CO_2 capture from flue gases (by reactive absorption with thermal solvent regeneration), renewable H_2 for CO_2 hydrogenation, compression work for gas compression in high-pressure methanol synthesis reactors and finally thermal energy for methanol separation (by distillation). Pearson et al. [20] have estimated that renewable hydrogen constitutes 65% of energy requirements in this CO_2-to-methanol process on well-to-tank basis. The remainder of energy requirements (35%) is associated with CO_2 capture (17%) and the compression work of reactants needed in the high-pressure methanol synthesis reactor (18%). Interestingly, another 2% is required for the separation of methanol from reaction products by distillation but this thermal energy can be extracted from the methanol synthesis reaction which is exothermic and generates comparable amount of thermal energy as needed in distillation. Consequently, CO_2-to-methanol processes require advanced energy integration to increase their cost-effectiveness [21,22]).

5. The complimentary role of biofuels and C-derived fuels to serve a transportation sector

The total sustainable technical potential of bioenergy in 2050 is projected to be between 80 and 170 EJ yr^{-1}. The midpoint value of this range, 125 EJ, is around one quarter of the current global energy use (about 500 EJ yr^{-1}) and less than one-tenth of the projected global energy use in 2050 (about 1300 EJ yr^{-1}). The global transport energy demand is about 100 EJ and is projected to grow to about 170 EJ in 2050. Assuming that half the available sustainable biomass energy was available for biofuel production at a conversion efficiency of 50% limits the substitution potential of biofuels to about 20% of the 2050 transport energy demand [20]. A slightly more optimistic position is adopted by the IEA with a prediction that 32 EJ of biofuels will be used globally in 2050, providing 27% of transport fuel [23].

Clearly, even though biomass production is expanding globally [24] bioenergy has limited capacity and therefore cannot meet all energy demands. Consequently, C negative fuels derived from CO_2 and renewable energy are of great importance for ensuring energy supply for expanding global economy. One another advantage of CCR is associated with energy storage opportunities of C-rich fuels in existing energy infrastructures, i.e. in a liquid fuel infrastructure (tanks) and in a natural gas infrastructure (grids, geological storage sites). Consequently, the present paper addresses C negative renewable energy technologies involving biomass or CO_2 as inputs as two complimentary technologies which enable to reduce C intensity of energy in all national energy systems.

6. C negative biofuels

Plants have evolved highly sophisticated light-harvesting mechanisms that allow for increased environmental tolerances and robustness, enhanced photo-efficiencies and prolonged lifetimes. Existing solar technologies such as PV or CSP still require expensive materials and achieve relatively low efficiencies of solar energy conversion. Therefore, green plants still have great potential for storing solar energy in biomass. Besides, bioenergy offers the provision of useful energy and one additional benefit associated with C management, i.e. bioenergy can be designed as C negative renewable energy technology.

Fig. 3 explains the main idea behind C negative bioenergy technologies involving C sequestration in vegetation and soil. It displays the cycle of energy and the cycle of C. In the energy cycle it is seen that solar energy is harvested during biomass growth, converted to useful forms of energy, utilized and released to the environment and finally it is emitted into outer space as infrared radiation. CO_2 is captured from the atmosphere by photosynthesis and then stored in biomass feedstock. During the conversion of biomass the C is converted to C-rich fuels and fertilizers. Fuels are combusted with subsequent release of a part of the C as CO_2. Fertilizers enrich soil C ensuring long-term storage of C in this C reservoir. The C stored in soil can be further mineralized to stable carbonates thus enabling permanent underground storage as C minerals.

Biomass is an abundant and renewable energy resource. It is second to fossil fuels in the world's energy consumption [25]. However, various bioenergy technologies are frequently characterized by different CO_2 intensities. Some bioenergy technologies are frequently criticized for their neutral or even C-positive characteristics. Others can offer significant net C reductions. Zhou et al. [25] have shown that low-input high-diversity grassland biomass offers net C reduction in the range from 6 to 17 Mg CO_2-eq ha^{-1} compared with only around 1 Mg CO_2-eq ha^{-1} estimated for corn grain ethanol and soybean biodiesel. It is thus central to identify these bioenergy technologies which can offer the greatest life cycle C reductions as well as explain main causes behind these reductions. Tilman et al. [26] have claimed that bioenergy done right must be derived from feedstocks produced with low GHG emissions and with little or no competition with food production. Accordingly, such feedstocks suitable for C negative biofuels include: (i) perennial plants grown on degraded lands abandoned from agricultural use, (ii) crop residues, (iii) sustainably harvested wood and forest residues, (iv) double crops and mixed cropping systems, and (v) municipal and industrial wastes. C negative liquid fuels offer more economic benefits such as the increase of energy security or enhancement for rural development and are particularly well-suited for under-developed and developing countries [27].

There are two central problems associated with bioenergy. The first problem is how to minimize the input of energy and thus indirect C emissions to cultivate biomass as well as indirect energy use. Therefore, expanded utilization of low-input high-diversity

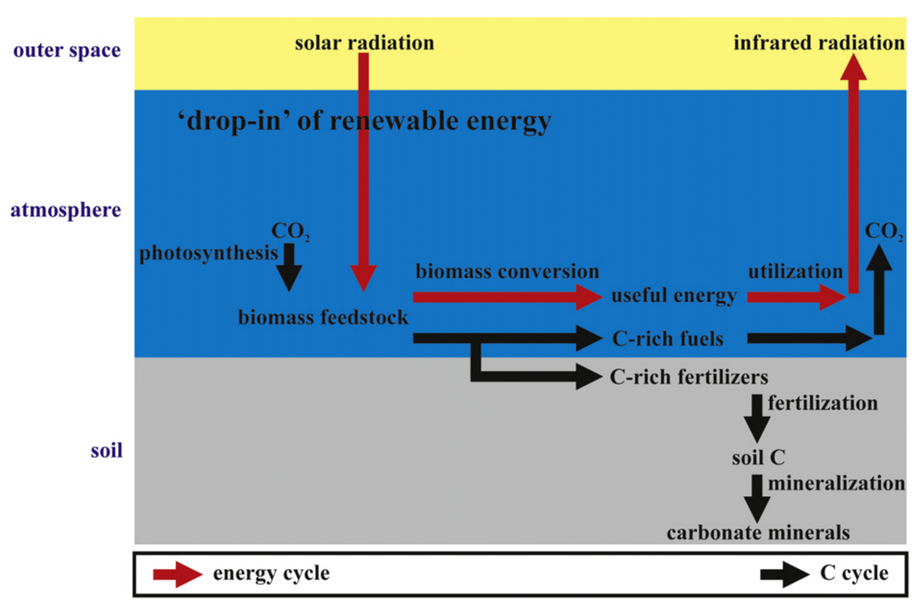


Fig. 3. Energy and C cycles in C negative biofuels.

grassland biomass which can minimize indirect energy use and C emissions seems a promising alternative [28]. The second problem is associated with increased N_2O emissions from agricultural soils because biomass cultivation often requires intensive synthetic N-fertilization [29]. The solution might lie in reduced use of synthetic N-fertilizers by increased waste biomass-derived organic fertilization and improved N efficiencies of agricultural practices. Han et al. [12] have recently indicated that in order to meet the US bioenergy goal of 30% in energy consumption by 2030 the expected large removal of N, P_2O_5 and K_2O from US land will necessitate an overall nutrient fertilizer application increase by a factor of 5.5 over the 1997 base line. This emphasizes that soil fertilization is central while developing sustainable bioenergy technologies. It is essential that such bioenergy technologies must not remove nitrogen, potash, phosphate and other nutrients from soil. Sustainable bioenergy technologies must extract useful energy from biomass but the remainder, e.g. anaerobic digestion-derived digestate, wood combustion-derived ashes, biomass pyrolysis-derived biochar which are rich in these nutrients must be returned back to soil thus ensuring nutrients and C recycling [30].

In summary if: (i) green plants which require little cultivation (fuel and agricultural chemicals) are used for biomass; (ii) a process is utilized that requires the input of very little energy to turn biomass into biofuel; and (iii) the CO_2, produced when biomass is turned into biofuel, is captured (in a low cost, practical manner) and sequestered long term (also in a practical manner) then photosynthesis pulls more CO_2 out of the atmosphere when the biomass is grown then is put back in all of the other steps. Below, important bioenergy technologies are described with emphasis put on how techniques allowing to achieve C negative effects.

6.1. Biogas

Anaerobic digestion (AD) is suitable for efficient conversion of wet biomass to two useful products: (i) biogas (CH_4+CO_2) and (ii) digestate (undigested biomass). Biogas [31–37] is generated via biological routes at relatively low-temperatures and thus thermal losses from AD units are beneficially minimized. Besides, low-temperature operation enables to recycle low grade thermal energy produced during biogas combustion back to AD units thus improving overall cycle thermal efficiency. Digestate comprises C-rich carbohydrates and N, K, P elements which concentrate during the AD. Hence, soil fertilization with digestate ensures both permanent deposition of atmospheric C in soil as well as the recycling of key nutrients back to soil [30].

Biogas can be also decarbonized by separating CO_2. CO_2 separation from biogas is a much more attractive option, than the separation of CO_2 from fossil fuel combustion-derived flue gases, because biogas comprises less impurities, such as particulate matter and NO_x. Further, biogas combustion-derived flue gases are very rich in CO_2 ($\sim$50%), in contrast to flue gases from air–coal combustion which have less than 15% CO_2. This CO_2-enrichment provides an opportunity for low cost CO_2 capture due to the increased driving forces in CO_2 separation processes. CO_2 is simply the ultimate form of biomass and thus CO_2 capturing in biomass-fuelled power plants seems particularly promising.

Below, three useful approaches are discussed which can allow for achieving more negative C intensity of biogas energy.

6.1.1. Biogas upgrading to biomethane with coproduction of C-rich fertilizers

When CO_2 is separated from biogas, the resulting biomethane has higher heating value (HHV) and is suitable for the injection into natural gas grids. The captured CO_2 is the fully oxidized form of C which is more suitable for soil storage than C in the form of carbohydrates in digestate. Interestingly, by applying reactive solvent scrubbing of CO_2 with solvents such as NH_4OH or KOH the main products obtained in this process are ammonium bicarbonate or potassium carbonate, respectively. Ammonium bicarbonate has been utilized by certain developing countries as a crop fertilizer for over 30 years with proved results in farmland practice, which enhanced crop root development and leaf growth [13]. As the gas injection into the natural gas grids requires high-pressure biomethane while solvent scrubbing processes benefit from elevated pressure operation due to increased separation driving forces, a high-pressure reactive solvent scrubbing (HPRSS) process is a particularly promising biogas energy technology [30].

6.1.2. Biogas enhanced by CO_2 recirculation

Capturing and recycling CO_2 [38] to AD units minimizes the conversion of biomass C to CO_2 during AD. Microorganisms operating under CO_2 enriched conditions still synthesize CH_4 while beneficially cease to synthesize CO_2. Consequently, the net production of CO_2 in CO_2-recirculating AD units can be reduced by a factor of 4 [39]. Such a process still produces flammable CH_4 gas but less CO_2 is formed thus selectivity to CH_4 is raised. As more C is now shifted toward methane and less CO_2 is formed, according to Eq. (1) more negative C intensity of energy is achieved. Additional benefit of the CO_2-recycled AD process is the removal of NH_3 from AD units since NH_3 inhibits methane fermentation [40].

6.1.3. Biogas decarbonization via oxy-reforming fuel cell (ORFC) cycle

A power cycle that can exploit CO_2 enrichment of biogas and thus achieve lower CO_2 separation costs is a biogas fuelled oxy-reforming fuel cell (ORFC) cycle, Fig. 4. In this power cycle biogas is converted to a mixture of CO_2 and H_2, which can be separated at lower costs than CO_2–N_2 or CO_2–CH_4 mixtures due to different separation properties of CO_2 and H_2 [41].

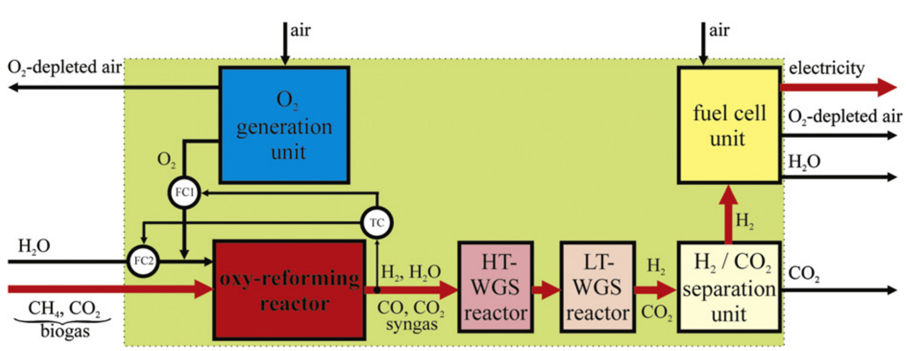


Fig. 4. Scheme of the biogas fuelled decarbonized ORFC power cycle.

The objective of the ORFC cycle is to split CH_4 by means of oxy-reforming reactions into free H_2 and simultaneously completely oxidize the remaining CO to CO_2. In order to avoid any dilution of reaction products by nitrogen, pure oxygen is supplied as an oxidizer. Therefore, the fully decarbonized ORFC cycle seeks improved conditions for separating a CO_2–H_2 mixture at the expense of using little oxygen as an oxidizing agent (around 0.35 mol O_2 per mol CH_4). Oxygen generation is beneficially integrated with a fuel cell unit and three reactors of the ORFC cycle.

According to the ORFC cycle CH_4 is split into CO and H_2 in the oxygen-steam atmosphere. CO is then oxidized to CO_2 providing energy for the endothermic CH_4 as well as H_2O splitting. H_2 is further separated and used as a fuel for electrically efficient H_2-fuel cells. By ensuring molar C/O ratio in the feeding mixture equal to 0.5 the overall reaction of the ORFC cycle can proceed with the formation of only CO_2 and H_2 (i.e. with no formation of CO and H_2O). When O_2/CH_4 ratio of 0.3412 [41] is adopted the process is autothermal, Eq. (2)

$$CH_4 + 0.5556CO_2 + 0.3412O_2 + 1.3176H_2O \leftrightarrow 1.5556CO_2 + 3.3176H_2 \quad \Delta H^{298} = 0 \text{ kJ/mol} \tag{2}$$

The ORFC process allows for the autothermal conversion of biogas into gas comprising 68%v H_2 and 32%v CO_2 [42]. Consequently, by utilizing the ORFC cycle H_2 can be autothermally produced from renewable biogas with the yield of 3.3176 H_2:CH_4 (on molar basis) and the remaining gas beneficially includes almost solely CO_2, i.e. is ready for CCR or CCS.

6.2. Liquid biofuels

The production of liquid biofuels can also be designed as C negative renewable energy technology. Similarly as biogas, liquid biofuels comprise mainly three elements: C, H and O. In contrast to biogas, liquid biofuels contain no CO_2 but instead they consist of organic compounds being a combination of C, H and O. The C/H ratio is greater than that in methane and the O content decreases energy content per unit mass. Several liquid biofuels such as ethanol produces CO_2 during fermentation which is conventionally released to the atmosphere. Besides, various liquid biofuels produce post-processing wastes which are suitable as organic C-rich soil fertilizers.

Below, three useful approaches are discussed which can allow for achieving more negative C intensity of liquid biofuels.

6.2.1. Pyrolysis bioils with coproduction of biochar as soil fertilizer

In pyrolysis solid biomass is converted to liquids, gases and chars, liquid fuel being the main target. Biomass pyrolysis pathway is today at research and pilot stage. Among pyrolysis technologies fast pyrolysis seems to be a potential candidate for power production in near term. Char obtained from biomass pyrolysis is known as biochar. Many research groups proposes to use biochar as soil fertilizer [43,44]. Biochar soil fertilization is the main driver for negative C intensity of this technology. However, biochar has higher heating value (HHV) greater than that of digestate. The reason is that C in biochar is not oxidized and therefore the biochar-based soil fertilization can be less economic than digestate fertilization. LCA estimates of biochar systems show that the net GHG emissions are typically negative amounting to −850 kg CO_2 equiv. per tonne dry feedstock [45].

Mathews [46] has indicated that microorganisms that fix nitrogen are encouraged by the addition of biochar to soil, and it has quite a spectacular impact on reducing the release of other nitrous oxide from agricultural soils. Therefore, the risk of N_2O emissions from agricultural soils utilized for energy crops with intensive N-fertilization [29] is minimized or avoided.

6.2.2. Cellulosic bioethanol characterized by low indirect C emissions

Cellulosic bioethanol contributes little to C emissions and has lower indirect energy consumption than corn-based bioethanol. This mainly originates from differences in biomass feedstock. Cellulosic biomass such as switchgrass, miscanthus or forest residues is a low-input biomass which requires less energy and C emissions to grow. Indirect C emissions [47] are therefore low and hence more negative C intensity of energy can be attained. Cellulosic bioethanol develops rapidly in many countries but still it is more expensive than starch bioethanol. The reason is that cellulosic bioethanol requires more advanced and complex processes such as pretreatment, enzymatic hydrolysis or gasification.

The need for pretreatment of cellulosic biomass increases the enzyme accessibility for improved digestibility of cellulose [48]. The fermentation step is a low-temperature process that has prospects for achieving high exergy efficiencies, i.e. of the order of 75–80% [49].

A significant progress in cellulosic bioethanol technologies is needed to improve cost-effectiveness of cellulosic bioethanol. When cost-effectiveness is ensured cellulosic bioethanol can develop as a promising route for C negative liquid biofuels.

6.2.3. Synthesis of biofuels from biosyngas derived from biomass gasification

Main idea behind making biofuels from biosyngas derived from biomass gasification [50] is little waste CO_2 emissions from the power cycle and significant amounts C-rich products. This ensures that negative C intensity of energy can be achieved. The target biofuels can be: bio dimethyl ether (bioDME), bio synthetic natural gas (bioSNG), bio Fischer–Tropsch (bioF–T) liquid fuels, biomethanol or bioammonia ($bioNH_3$). Clausen et al. [51] have reported that bioDME can be obtained from torrefied woody biomass with energy conversion efficiency of 58–71%. Juraščík et al. [52] have claimed that bioSNG can be obtained from woody biomass with exergetic efficiency of 70-72%. Carbo et al. [53] have proposed a process for more C negative bioSNG from biomass by integration with CCS. The process is advantageous due to the achieved net production of water, in contrary to fossil fuel power plants with CCS. The produced water is removed during bioSNG upgrading, and is therefore relatively clean, which makes waste water treatment more cost-effective. Sarkar et al. [54] have analyzed economics of the conversion of biosyngas derived from forest residues to biofuels: bioF–T fuels, biomethanol, bioammonia, and bioDME but the costs of these fuels are today greater than their fossil fuels-derived counterparts. This emphasizes that a significant progress in bioenergy must be made before these technologies will be suitable for commercial scale deployment.

The 'drop-in' of additional, i.e. of non-biomass origin, renewable energy is a useful approach to intensify the conversion yield of biomass C into fuel C. Seiler et al. [55] have demonstrated that the enhancement of a biomass gasification process by external energy inputs (under allothermal conditions) can multiply the conversion yield of biomass C into fuel C by a factor of 3 in comparison with existing (autothermal) gasification processes.

6.3. Algae—third-generation biofuels

Algae [56] have great potential for the recycling of CO_2 for the synthesis of algal biomass. The interest in CO_2-to-algae routes originates from fast growth of this plant and relatively efficient use of solar energy. The existence of various algae species creates wide range of potential applications for algae. It should however

be emphasized that the significant drawback in all the technologies involving this group of organisms is the big share of cost for algae cultivation. Therefore, today algal biomass is unsuitable to cultivate it solely for bioenergy applications and must be integrated with the production of other value-added products e.g. pharmaceutics, cosmetics, food, etc. while only organic wastes should used in bioenergy applications. Unfortunately, processes for the recovery of complex molecules from algal biomass are expensive and a significant technological progress is required before commercial deployment.

The potential algae yield is limited by low CO_2 concentration in air (0.04%v) which decreases the economic feasibility of algae farming [57]. Therefore, CO_2 capture from flue gas emissions from power plants that burn fossil fuels achieves better recovery due to the higher CO_2 concentration of about 15% in flue gases from coal-firing and 35% in biogas. To capture the CO_2 emissions of a 1 MW power plant, an algal plant of about 65 ha would be necessary for coal-firing while an approx. 22 ha algal plant would be sufficient for biogas production. A number of microalgae species are able to assimilate C from soluble carbonates such as Na_2CO_3 and $NaHCO_3$ [57] which creates one another opportunity to supply C to algae farming.

Below, two useful approaches are discussed which can allow for achieving more negative C intensity of algae.

6.3.1. Removal of CO_2 by algae cultures

Kao et al. [58] have demonstrated the ability of a mutant strain of the microalga *Chlorella sp.* to capture CO_2 in the process of biogas upgrading to biomethane. Under the investigated conditions algae cultures were aerated with desulfurized biogas ($H_2S < 50$ ppm). The efficiency of CO_2 capture from biogas of 50% was achieved, and the CH_4 concentration in the effluent load of 80% was obtained. This technique emphasizes the need for integrating biogas plants with algae farms because significant economic and C reduction synergies are possible. Namely, algae capture CO_2 from AD units and produce high quality fast growing biomass. In this way a significant C negative intensity of energy is ensured.

Cerón-García et al. [59] have investigated the production of biodiesel with waste glycerol as the carbon source and with waste gaseous CO_2 as the pH controlling agent in algae reactors. This technology allows for particularly promising C management because it uses two sources of waste carbon as the input.

6.3.2. Pyrolysis of algae to bioils and biochar as soil fertilizer

Yet another opportunity includes the integration of algae farms with pyrolysis of algae biomass to bioils and biochar [46]. This technology would require advanced thermal integration but theoretically could ensure significant negative C intensity.

6.4. C sequestration strategies in vegetation and soil

The addressed bioenergy technologies sequester C in vegetation (during biomass cultivation) and in C-rich products such as fuels, fertilizers, etc. (target products for input C). The use of fertilizers leads to C storage in soil.

6.4.1. C stored in vegetation

Expanded cultivation of biomass can increase the potential of storing C in vegetation. Forests are one important example of the largest manageable C sinks on Earth. Afforestation could increase the availability of woody biomass for bioenergy applications. Economic benefits are possible through the value of forest products and through the long-term social and environmental benefits that include improved soil and air quality, reduced surface run-off and erosion, and ecosystem health. The amount of C stored is determined by forest management practices, such as tree species, geographic location, and characteristics, and through the disposition of forest products. The cost includes that associated with additional land, planting, and management, and secondary costs or benefits such as non-climatic environmental impacts or timber production. C sequestration as biomass can be prolonged through the use of wood as furniture and other housing materials. Disadvantages linked with afforestation include relatively slow growth of trees and large land occupation.

6.4.2. C stored in soil and the role of C mineralization

Soil is suitable for storing C derived from the non-harvested parts of plants, digestate or biochar. This C sequestration intensifies negative C intensity of bioenergy, since only a part of the biomass C processed. The balance is allowed to stay in soil as SOC. Soils can store large but limited amount of C. Therefore, C mineralization in soil is considered as a promising route to turn soil organic C into stable minerals (carbonates) and thus significantly increase the permanence and capacity of terrestrial C storage.

Mineralization by properly selected higher plants exhibits the great promise for enhancing cost-effective terrestrial C sequestration for long-term periods. Hundreds of plant species (forest trees, shrubs, subshrubs, herbs, and crop plants) are known to mineralize directly atmospheric CO_2 [59]. The great benefit of cultivation of such plants is therefore mineralization of atmospheric CO_2 with low costs. An example of studies on mineralization of C in terrestrial ecosystems is the tropical iroko tree (*Milicia excelsa*) which has a high ability of accumulating mineral C as calcium carbonate [60].

The formation of minerals from soil C is widespread among animals which create their body structures such as bones, teeth or shells. Lifeless animals thus contribute to the permanent deposition of mineralized C in soil. Further, some kinds of earthworms have calcium glands which enable them to neutralize consumed acidic organic substrates from soil. During this neutralization process earthworms secrete granules of calcium carbonate into soil [61]. Lambkin et al. [62] have reported that in 11 various soils earthworms secreted on average 0.8 mg $CaCO_3$ earthworm^{-1} day^{-1}. Assuming 15 $CaCO_3$ secreting earthworms per m^2 of soil and 4.8×10^{13} m^2 of arable land worldwide it can be calculated that the global potential of C mineralization by Ca-secreting earthworms is about 0.25 Pg C yr^{-1} which is around 3% of anthropogenic atmospheric C emissions to be obtained only by harnessing earthworms.

Another attractive opportunity for C mineralization arises from the role played by microorganisms in soil which also can mineralize SOC. Biosphere microorganisms can efficiently induce carbonate precipitation and thus contribute to the formation of stable minerals [63].

Renforth et al. [11] have shown that 0.29 Pg C yr^{-1} can be sequestered in soils through chemical mineralization by implementing waste Ca-containing industrial minerals (crushed concrete, etc.).

In general, the potential for the mineralization of C in soils remains mostly unused and therefore this option must be seriously considered in near future.

7. C negative fuels derived from CO_2 and renewable energy

Renewable energy resources often are relatively unstable and therefore renewable energy systems require energy storage. CO_2 capture and recycling (CCR) technology is an ideal candidate for storing renewable energy in the form of useful fuels and, at the same time, the CCR can lead to the net removal of CO_2 from the

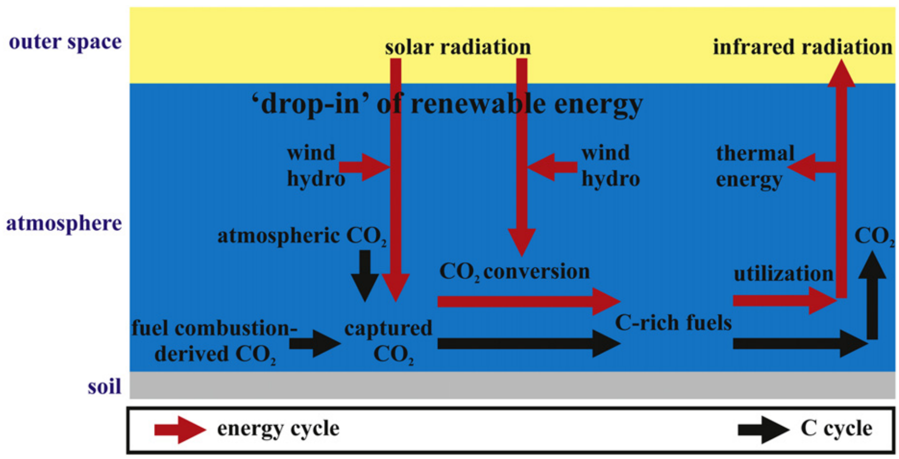


Fig. 5. Energy and C cycles in C negative fuels derived from CO_2 and renewable energy.

atmosphere. The CCR allows for storing renewable energy in the form of useful C-rich energy carriers which can compete with fossil fuels, at least in transportation energy applications.

Fig. 5 explains the main idea behind C negative fuels derived from CO_2 and renewable energy. Fig. 5 displays the energy cycle and the C cycle. In the energy cycle it is seen that any renewable energy (solar, wind, hydro, etc.) is harnessed to drive the process of capturing CO_2 and the process of recycling CO_2 to C-rich fuels. Further, the stored fuel energy is utilized and released to the environment. A part of released energy is emitted into space as infrared radiation and the reminder remains in the environment often as thermal energy and thus compensates energy taken from the environment by renewable technologies such as wind or hydro. In the C cycle it is seen that CO_2 is captured from the atmosphere or is derived from fossil fuel combustion. Further, CO_2 is converted to C-rich fuels in order to store renewable energy. Finally, C-rich fuels are combusted thus releasing CO_2 back to the atmosphere.

As CO_2-emitting utilities and other industries move toward implementing C capture and storage (CCS) technologies to manage their GHG emissions, more and more CO_2 will become available as a resource for multiple energy applications. CO_2 will be a plentiful potential feedstock (C source) for many products, including fuels. CO_2 can also be captured directly from the atmosphere. Further, by harnessing renewable energy CO_2 can be converted to C-rich fuels and other C-rich products. However, many CO_2 conversion technologies seem not fully economical today. The reason is associated with process thermodynamics and slow kinetics of CO_2 conversion [64]. The fundamental challenge is the conversion of CO_2 into carbon monoxide (CO) by removing oxygen atom from the CO_2 molecule. Since the CO_2 is a very stable molecule, conversion processes need a lot of energy. The required energy can be taken from solar, wind or hydro power via photochemical/catalytic, thermochemical/catalytic, electro-chemical/catalytic or bio-chemical/enzymatic processes.

CCR receives increasing attention in the academic literature and is addressed through R&D projects supported by the United States Department of Energy (DOE) and under EU's 7th Framework Programme. The US DOE supports CCR projects falling into the categories of: (i) enhanced hydrocarbon recovery, (ii) chemicals production, (iii) mineralization processes for building products, and (iv) plastics production [65].

CCR directed at the synthesis of fuels from CO_2 and renewable energy seems particularly promising because of growing global demands for transportation liquid fuels and limited oil reserves. However, a huge progress is needed to overcome thermodynamic and kinetic limitation in the CO_2 conversion step. In general, any chemical conversions are driven by differences in the Gibbs free energy between the reactants and products of a chemical reaction (under certain conditions), as shown by the Gibbs–Helmholtz relationship

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

Any attempt to use CO_2 as a feedstock must take close account of the relative stability of the ultimate reaction products, as compared to the reactants. Both terms (ΔH^0 and $T\Delta S^0$) of the Gibbs free energy are usually not favorable in converting CO_2 to other molecules. The C–O bonds are relatively strong and substantial energy must be input for their cleavage in terms of C reduction. Moreover, ΔG^0 only provides information as to the yield of products at equilibrium through the relationship $\Delta G^0 = -RT \ln K$. However, even if favorable thermodynamic equilibria for CO_2 conversion could be ensured through raising T, the kinetics of such a process still might be unfavorable for its practical realization. Indeed, kinetics of many CO_2 conversions are very slow. Therefore, any progress in the use of CO_2 as a useful reactant, e.g. towards fuel synthesis, will only emerge through use of advanced catalytic or electrochemical approaches.

The option of CO_2 recycling to fuels must be seriously considered by policy makers as an energy decarbonization strategy because the potential of biofuels is limited, first because of limited biomass availability (see Section 5), second because of suggested increased N_2O emissions from energy crop cultivation. According to Crutzen et al. [29] these N_2O emissions can even negate global warming reductions expected from fossil fuel replacement by biofuels. Fuels synthesized from CO_2 and renewable energy are therefore particularly promising in the GHG constrained world at least for the transportation sector.

7.1. Fuels derived from CO_2 and renewable solar energy

Concentrated solar radiation can be used to synthesize fuels from CO_2 and H_2O [66,67]. Due to unfavorable thermodynamic equilibria solar thermochemical splitting of CO_2 and H_2O must be operated at high temperatures. Solar fuel synthesis can utilize the entire solar spectrum, and as such provide an attractive path to solar fuels production with high energy conversion efficiencies. CO_2/H_2O can be converted to fuels through direct thermolysis. Alternatively, two-step thermochemical cycles that use metal oxide redox reactions can be involved. The two-step solar-to-fuel technology can bypass the CO/O_2 or H_2/O_2 separation problem. Fig. 6 shows schematically the two-step CO_2/H_2O splitting thermochemical cycle based on metal oxide redox reactions. The net reactions are $CO_2 = CO + 0.5O_2$ and $H_2O = H_2 + 0.5O_2$. Since

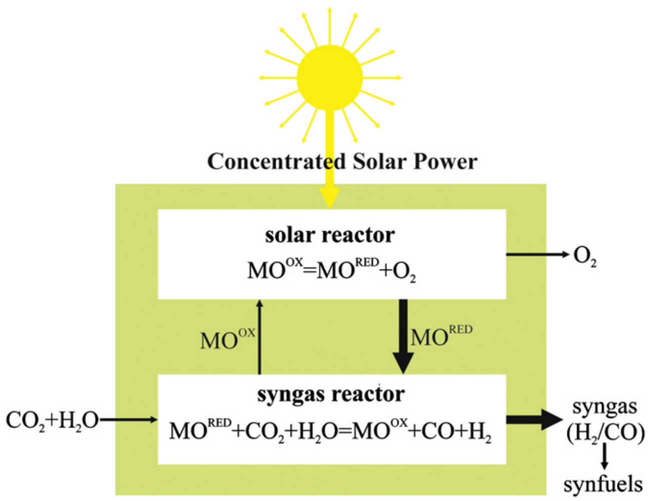


Fig. 6. Two-step solar thermochemical cycle for CO_2/H_2O splitting based on metal oxide redox reactions. Notations: MO^{OX}, metal oxide; MO^{RED}, the corresponding reduced metal or lower-valence metal oxide.

O_2 and CO/H_2 are released in separate reactors, the need for high-temperature gas separation is thereby eliminated. The syngas mixture (CO/H_2) can be further processed to liquid hydrocarbon fuels, such as diesel, kerosene, methanol, and gasoline using existing conventional technologies, e.g. F–T.

Cerium oxide (ceria) has emerged as a highly attractive redox active material because it displays rapid fuel production kinetics and high selectivity. Reduction proceeds via the formation of oxygen vacancies and the release of gaseous O_2, resulting in the subsequent change in stoichiometry (x). Oxidation is capable of proceeding with CO_2 and/or H_2O, thereby releasing CO and/or H_2 and re-incorporating oxygen into the lattice. The two-step CO_2/ H_2O splitting solar thermochemical cycle based on oxygen-deficient ceria is represented by

$$\text{High-}T\text{ reduction step}: CeO_2 \rightarrow CeO_{2-x} + 0.5xO_2 \tag{4}$$

$$\text{Low-}T\text{ oxidation step}: CeO_{2-x} + xCO_2 \rightarrow CeO_2 + xCO; CeO_{2-x} + xH_2O \rightarrow CeO_2 + xH_2 \tag{5}$$

Chueh et al. have reported that solar-driven high-temperature thermochemical cycles can attain maximal solar-to-fuel efficiencies of around 0.8% [67].

Photocatalytic reduction of CO_2 [68] mimics photosynthesis as it converts light to chemical energy of organic compounds (here fuels) and oxygen. It could emerge from laboratories and be trialed at a commercial stage within next few years. Significant challenges still remain on the scaling up of this technology. Achieved conversions rates of up to 25% at a laboratory scale are promising but need further improvement. Then the technology would have to be scaled up to see how economical it can be. Main challenges are associated with the design of systems utilizing the entire solar spectrum and suitable catalysts.

Uner and Oymak [69] have found that the rate of artificial photosynthesis over Pt–TiO_2 catalyst is limited by the water splitting reaction. Besides, the deposition of carbonaceous intermediates followed by catalyst deactivation is a significant problem and as the authors have reported H_2 addition is needed to remove C deposits by C methanation. The authors have reported that the rates of catalytic reaction are still 6–7 orders of magnitude behind the rates of waters splitting in the photosynthetic cells [70]. Therefore, catalyzed artificial photosynthesis requires significant improvement before it can be commercially deployed.

7.2. *Fuels derived from CO_2 and renewable hydrogen*

Replacing water by renewable hydrogen [71] is promising because CO_2 hydrogenation is one of the most thermodynamically and kinetically attractive approaches to CO_2 conversion. CO_2 hydrogenation allows for synthesis of various fuels such as methanol, dimethyl ether (DME), higher alcohols or formic acids [72]. Wang et al. [73] have shown that catalytic hydrogentation of CO_2 is a powerful process in CO_2 conversions. The CO_2 methanation reaction is thermodynamically favorable ($\Delta G^{298\ K} = -130.8$ kJ mol^{-1}). However, the reduction of the fully oxidized C to methane is an eight-electron process with significant kinetic limitations, which thus requires a catalyst to achieve acceptable rates and selectivities [74].

7.2.1. *Dimethyl ether (DME)*

DME can be produced from CO_2 hydrogenation through methanol (MeOH) synthesis followed by methanol dehydration, known as the two-step process. Alternatively, the two processes can take place simultaneously within one reactor using a bifunctional catalyst. The one-step DME process can achieve a higher CO_2 conversion with little methanol yield. The one-step DME synthesis requires moderate temperatures of up to around 530 K.

In CO_2 hydrogenation, there is competition between the reverse WGS reaction and methanol and DME syntheses reactions. The WGS reaction reaches thermodynamic equilibrium fast [75], while the methanol and DME syntheses reactions are much slower [76]. CO, which is a product of the reverse WGS reaction, will be therefore present in the product due to the fast rate of the WGS reaction. From a consideration of C source utilization, the CO in the outlet stream should be separated from the DME and methanol and recycled back into the reactor. As DME synthesis is controlled by the kinetics rather than by thermodynamics [77,78] suitable catalysts are critical for DME production. In DME processes CO_2 conversion around 30% and DME yield around 20% are achieved [79]. Therefore, the costs of recirculation of unconverted substrates and that of separation are important.

7.2.2. *Methane*

Sharma et al. [80] have claimed that CO_2 hydrogenation to methane can be more effective than DME synthesis. Their results showed 55% conversion of CO_2 with 99% selectivity to methane. The process was realized on Ru-doped ceria catalyst.

Sterner [81] has also studied CO_2 methanation process. The renewable power-to-methane efficiency is predicted to be 48% using measured energy values for capture and concentration of CO_2 from air of 430 kJ/mol.

7.3. *Fuels derived from CO_2 and renewable electricity*

Fuel synthesis from CO_2 and renewable electricity is also promising because the CO_2 conversion step can be realized via electrochemical CO_2 reduction. The electrochemical reduction enables to overcome a key problem arising during CO_2 conversions, i.e. the reduction of CO_2 to CO. The direct electrochemical reduction of CO_2 [82] may allow for a simple process by avoiding high temperature reactors. Electrochemical conversion can be performed at room temperature and ambient pressure. A renewable source of electricity can be used to drive the process, including solar, wind, hydroelectric, geothermal, tidal, and thermoelectric processes. The target fuels are CO, formic acid and methanol. Especially formic acid and carbon monoxide require little energy input compared to their respective market values.

Current research is yielding catalysts with long-term performance characteristics and low energy use, but significant technical

advances are still needed for large-scale use. Electrochemical conversion promises to be deployable in many systems, because of its low footprint, its scalability, its fungible use of electricity, and its ability to produce many value-added products [83]. The combination of the electrochemical process with grid-based ancillary services can make these processes economically viable. The working principle of an electrochemical reactor for CO_2 conversion to formate/formic acid is schematically presented in Fig. 7.

Graves et al. [84] have indicated that high-temperature electrolysis (1120 K) using solid oxide cells appears to be one of the most promising pathways to dissociate CO_2 to CO and simultaneously split water to H_2. By applying high temperatures both thermodynamic equilibria and reaction rates are improved. With increasing temperature, a larger portion of heat and corresponding smaller portion of electricity is needed for the dissociation. Heat at moderate temperatures can be provided at low cost and can originate from renewable sources and from Joule heating effects of the electrolyzer. Further, high-temperature cells nearly always have lower internal resistance than low-temperature cells which minimizes thermal losses. High temperature activates catalytic reactions. The main problem associated with high-temperature electrolyzers is the intermittent nature of renewable sources. If the high-temperature process is driven by an intermittent power source, the efficiency will likely be somewhat lower. For example, if the electrolyzer is driven by solar power, the cells must either be heated up and cooled down each day (thermal cycling) or kept hot throughout the night, and they should be kept hot during power supply interruptions (e.g. due to clouds). This extra heating uses energy, lowering net efficiency and necessitating advanced thermal management.

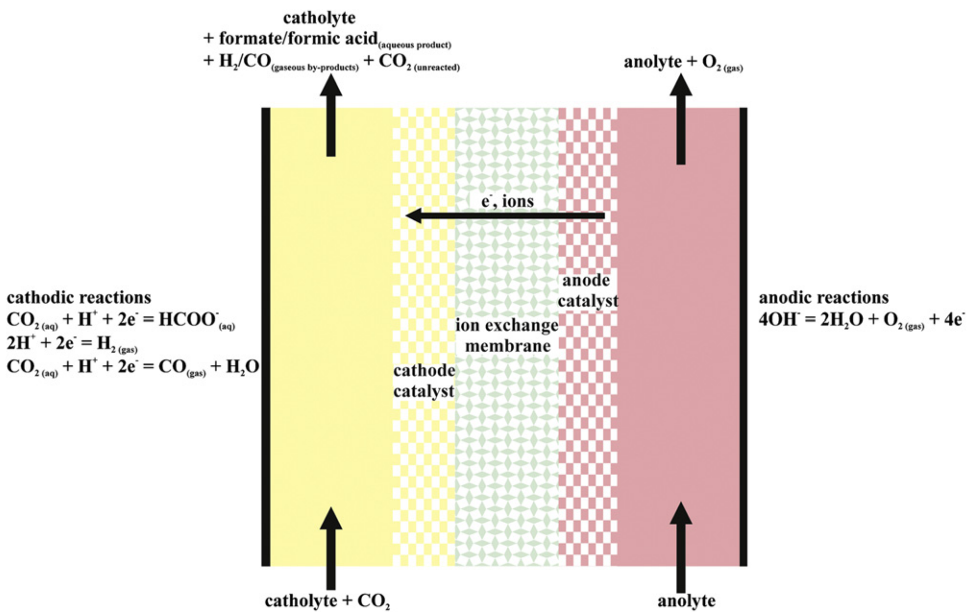


Fig. 7. Schematic of an electrochemical reactor for the conversion of CO_2 to formate/formic acid.

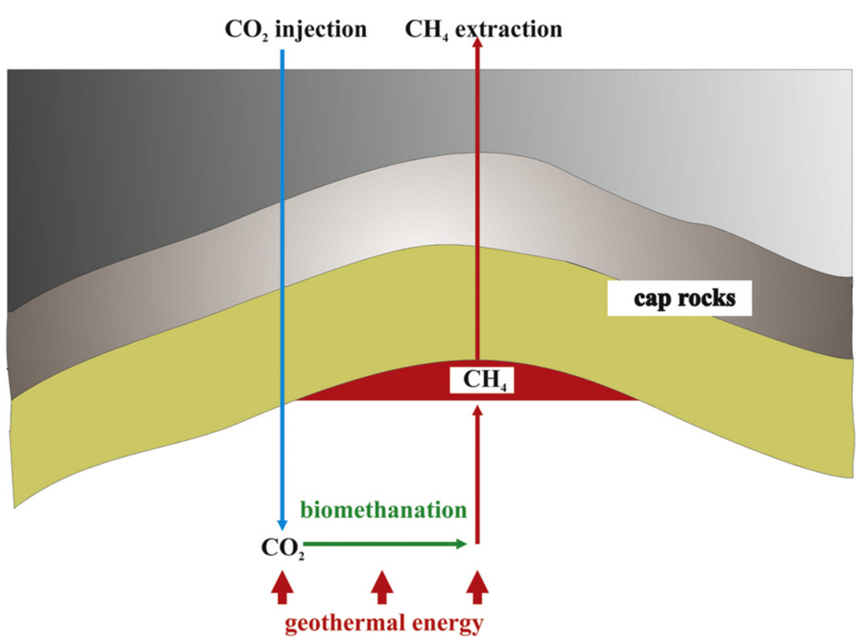


Fig. 8. Underground reactor for biogenic methane from CO_2 and completely free geothermal energy.

7.4. *Fuels derived from CO_2 and renewable thermal energy*

Renewable thermal energy can be provided at relatively low cost and therefore thermal energy-driven cycles for CO_2 recycling to fuels are of interest.

7.4.1. *Trireforming*

The treatment of flue gas from fossil-fuel fired power plants by trireforming could become an attractive approach for converting the CO_2, H_2O and O_2 contained in the flue gas via synthesis-gas processing into fuels, such as methanol. In the trireforming process the dry reforming of methane with CO_2, steam reforming and the partial oxidation of methane occur simultaneously. Unfortunately, thermal conversion of CO_2 is feasible at very high temperatures which impose constraints on such technologies and decrease their fuels-to-thermal energy efficiencies.

7.5. *Fuels derived from CO_2 and renewable geothermal energy*

Geothermal energy is available in many regions but often it is as a low-temperature heat source. Suitable technologies aimed at utilization of this renewable resource for CO_2-to-fuel conversions is thus of interest.

7.5.1. *Biogenic methane*

Biogenic methane is a term used to describe methane-rich gas derived from the underground reduction of CO_2 via biogeochemical processes, Fig. 8. Biogenic methane can be obtained from geologically stored CO_2 in depleted oil and gas reservoirs, with subsequent conversion of the CO_2 to CH_4 via e.g. microorganisms. It is thus a sort of an underground fuel reactor which is driven by free geothermal energy. The conversion of CO_2 includes methanogenesis, hydrogenogenesis and geochemical processes [85]. Such processes are pervasive in nature. Kawaguichi et al. [86] have recently reported experimental results on the methanogenic activity of *Methanothermobacter thermautotrophicus* under conditions relevant to geological CCS reservoirs. However, the processes which contribute to the methane production are complex, still poorly understood and hence further studies of this technology are needed. There are also problems with the selection of appropriate sites for this process. Today no researches can demonstrate that biogenic methane can be obtained with sufficient kinetics ensuring cost-effectiveness and technical feasibility of this technology.

7.6. *Additives derived from CO_2 and renewable chemical energy*

CO_2 can also be converted by utilizing renewable energy stored in chemicals as chemical energy.

7.6.1. *Carbonation*

Although C in CO_2 molecule is at its highest possible oxidation state and no further oxidation is feasible, the CO_2 can react with some other molecules via thermodynamically favorable routes even with the release of thermal energy. One example of such relatively rare processes is the CO_2 carbonation reaction. This thermodynamically favorable and exothermic process [87] makes use of the fact that CaO has very high content of chemical energy which allows for the progress of the CO_2 carbonation reaction. Therefore, in carbonation-based CCR processes renewable energy is needed only for the CO_2 capture step. It must be however noted that the production of CaO from natural minerals requires a lot of energy.

CO_2 carbonation requires little renewable energy because it is an exothermic process. The bicarbonates produced from the mineralization process can be sold and used for a variety of purposes, such as an additive to animal feed and to ponds growing algae. The process operates at energy efficient conditions, thereby reducing CO_2 emissions in two ways: by direct mineralization with CO_2 that would otherwise be emitted in flue gas and by avoidance of CO_2 by producing chemicals using a process that is less energy intensive than conventional commercial processes.

8. Conclusions

According to International Energy Agency global carbon intensity of total primary energy supply in 2009 was 1.54×10^{-5} g C J^{-1} which corresponds to the increase of atmospheric CO_2 content by 2 ppmv yr^{-1} or by 0.5% v yr^{-1}. Therefore, carbon intensity of energy must be urgently significantly decreased in order to stabilize the content of CO_2 in the atmosphere [3] and prohibit unwanted climate change.

This review paper analyzed technological options which could negate carbon intensity of some renewable energies. Two large groups of potential carbon negative renewable energy technologies were approached: (i) carbon negative biofuels and (ii) carbon negative products derived from CO_2 and renewable energy. Technologies from both these groups must be seriously considered for near-term deployment because according to International Energy Agency biofuels can provide only up to 27% of transportation fuels demands by 2050. The remainder of 63% demands would have be met in a significant part by fuels derived from CO_2 and renewable energy.

In the first group of carbon negative renewable energy technologies—carbon negative biofuels, the biogas energy was identified as the most mature and relatively cost-effective option. The emphasis in future R&D must be however put on various sophisticated carbon management strategies which could enable to achieve more negative carbon intensity of biogas energy while retaining cost-effectiveness. The expounded technological options which allowed for achieving more negative carbon intensity of biogas energy included: (1) biogas upgrading to biomethane with coproduction of carbon-rich fertilizers (fertilizers were coproduced from CO_2 captured from biogas fuel and thus carbon was recycled to soil), (2) biogas generation enhanced by CO_2 recirculation (the addition of the recycled CO_2 to AD units promoted methanation over CO_2 synthesis and hence the selectivity of carbon-to-methane was increased by a huge factor), and (3) biogas decarbonization via oxy-reforming fuel cell (ORFC) cycle (allowed for oxy-fuel conversion of biogas to renewable H_2 and subsequent disposal of the remaining, high purity CO_2). Liquid biofuels technologies could also be refined to achieve negative carbon intensity of energy. Namely, pyrolysis of biomass could benefit from coproduction of biochar, i.e. a promising soil amendment. Bioethanol obtained from low-input cellulosic biomass was demonstrated to have low indirect carbon emissions. Biomass gasification could be enhanced by converting biosyngas to various liquid biofuels. Algae energy could negate carbon intensity by integrating algae farms into biogas plants and utilizing the removal of CO_2 from biogas by algae cultures. Also algae biomass could be pyrolyzed to biochar.

In the second group of carbon negative renewable energy technologies—carbon negative fuels derived from CO_2 and renewable energy, the technologies were discussed with respects to all existing categories of renewable energy. It was demonstrated that renewable solar energy could be used for converting CO_2 via thermochemical cycles which allowed for avoiding complex high temperature oxygen separation from thermal decomposition products. Renewable hydrogen was demonstrated as a very

reactive agent and energy carrier promising in hydrogenation of CO_2 to hydrocarbons such as DME and methane at relatively low temperatures. The demonstrated advantages of renewable electricity were associated with the ease of converting CO_2 at very low temperatures and pressures via electrochemical cycles. Renewable thermal energy found to be less efficient in CO_2 recycling but instead this energy carrier could be often provided at very low cost. Further, an opportunity to use entirely free geothermal energy (without the need to extract it aboveground) was demonstrated in order to convert CO_2 into biogenic methane. Finally, the potential of renewable energy in the form of chemical energy was discussed as a useful energy carrier for converting CO_2 via carbonation cycles to useful carbonate and bicarbonate products.

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